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Abstract

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Keywords

Ames Laboratory, synchrotron radiation, valence plasmon

Disciplines

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Comments

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Thermomodulation Study of Plasmons and Longitudinal Excitons in Alkali Halides*

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Thermoreflectance measurements on LiF and KCl were made from 10 to 30 eV using synchrotron radiation. Analysis of the differential dielectric and electron-energy-loss functions shows that the energy-loss peak generally attributed to the valence plasmon actually arises from the plasmon and overlapping longitudinal-exciton-like peak(s).

Different interpretations have been proposed for the strong peak in the electron-energy-loss spectra on the high-energy side of the fundamental absorption edge of alkali halides. The first was to associate it with the plasma resonance of the valence electrons.¹⁻³ The dielectric function, $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$, has the behavior characteristic of a free-electron gas: ϵ_1 crosses zero with positive slope and ϵ_2 is small, decreasing with increasing energy. The energy of the loss peak is higher than the free-electron plasmon energy, $\hbar\omega_p$, calculated for 6 electrons per molecule. This shift is due to the presence of interband transitions at lower energies.⁴ Sueoka⁵ measured the angular dispersion of the loss peak in LiF (25.3 eV) and found a strong plasmonlike dispersion. A totally different dispersion was found by Creuzburg and Raether,⁶ who found essentially no momentum dependence, as expected for single-particle excitations. They concluded that the loss peak is determined by one-electron transitions. A third interpretation considered both the peak in ϵ_2 and that in $\text{Im}(-1/\tilde{\epsilon})$ as arising from the simultaneous creation of two excitons.^{7,8} As expected, the peak in ϵ_2 occurs at an energy approximately twice that of the first exciton peak. The calculated shift of the loss peak toward higher energies is in agreement with experiment. Gout and

Pradal⁹ found the 25.3-eV loss peak actually had two components. Antinori, Balzarotti, and Piacentini¹⁰ noticed that the structure in $\text{Im}(-1/\tilde{\epsilon})$ is connected with the one in ϵ_2 . They found for KBr that the energy-loss function calculated by fitting the ϵ_2 peak with a Lorentzian oscillator peaks at the same energy as the experimental one. In several alkali halides the peak in ϵ_2 shows a multiplet structure as does the loss peak. In such cases the high-energy component of the loss structure has been associated with the plasma resonance and the other with interband transitions.⁹ LiF is unique, for ϵ_2 shows a single feature at 23 eV¹¹ while the energy-loss structure is double.⁹

No additional experimental data exist so far to test these interpretations. Since most of the alkali halides show these features, they probably have a common origin. We measured the thermoreflectance (TR) of several alkali halides between 12 and 30 eV, where these structures are present. By means of Kramers-Kronig analysis, we obtained the thermomodulation (TM) differential optical constants $\Delta\tilde{\epsilon} = \Delta\epsilon_1 + i\Delta\epsilon_2$, and $\Delta[\text{Im}(-1/\tilde{\epsilon})]$ the differential electron-energy-loss function (ΔEEL).

The experimental technique¹² will be described in detail elsewhere. Synchrotron radiation emitted

by the electrons orbiting in the storage ring of the Synchrotron Radiation Center of the University of Wisconsin was used as a light source. The samples, freshly cleaved single crystals or evaporated films, were indirectly heated with a unipolar square-wave current of about 2 W peak through a Mo film. Two different frequencies were used, 1.6 Hz with an analog lockin system, and 0.1 Hz with a digital lockin system. The average temperature of the samples during measurements was about 200 K.

The results obtained for LiF will be discussed in detail. Since the 12–30-eV range covers all the fundamental absorption spectrum of LiF, we can compare the results obtained for the 25-eV peak in ϵ_2 with those obtained for the first exciton. Moreover, the peak in ϵ_2 is single, so that the plasmonlike feature is well separated from the interband structure. We shall present also results on KCl as an example of a multiple interband structure superimposed on the plasma resonance.

A single oscillator, with asymmetric Lorentzian line shape, fits the first exciton peak in ϵ_2 in several alkali halides.^{13–16} The TM $\Delta\tilde{\epsilon}$ of LiF can be reproduced very well by shifting the oscillator resonance energy to higher energy at lower temperatures as shown in the left portion of Fig. 1. The temperature dependence of the linewidth

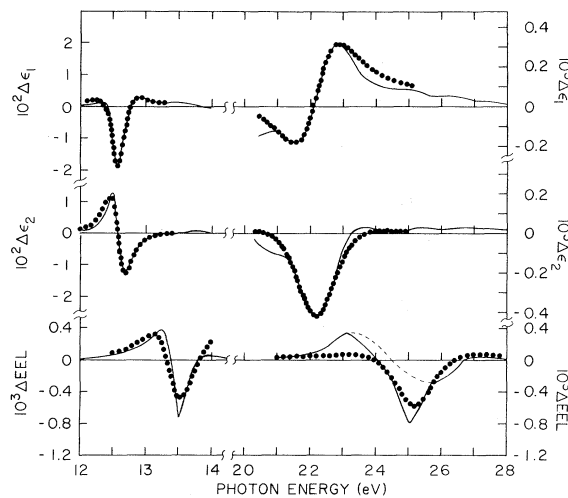


FIG. 1. Differential real and imaginary parts of the dielectric function, $\Delta\epsilon$ and $\Delta\epsilon_2$, and differential electron-energy-loss function, ΔEEL , for LiF obtained by a Kramers-Kronig analysis of thermoreflectance data. Note break in energy scale and different ordinate scales. The points are computed, as described in the text. The dashed line is described in the text.

was found to give only a small correction. This result can be extended to the other alkali halides, since the TR spectra around the first exciton peak measured for other alkali halides by Nosenzo, Reguzzoni, and Sammogia¹⁶ are very similar to our result. Associated with the exciton peak in ϵ_2 at energy E_{0T} there is a peak in the loss function at a higher energy E_{0L} . This feature is very well understood and is associated with a longitudinal exciton.⁹ The longitudinal-transverse exciton splitting is given by^{17,18} $E_{0L} - E_{0T} = (\hbar\omega_p)^2 f / (2\epsilon_c E_{0T})$, where f is the oscillator strength and ϵ_c is an effective dielectric constant which contains contributions from all other transitions. In this case they occur at higher energies only. Using $\epsilon_\infty = 1.92$ for ϵ_c , the calculated splitting is 1.04 eV, in agreement with the experimental value of 0.9 eV.

Let us now concentrate on the high-energy structure in ϵ_2 and the loss function. The differential optical constants for LiF are shown in the right side of Fig. 1. The feature in $\Delta\tilde{\epsilon}$ is single. The peak³ in ϵ_2 was reproduced with a symmetric Lorentzian of 1.1 eV half-width. The calculated line shape, shown by the dots in the right side of Fig. 1, was obtained by *changing only the line-width. No shift at all of the peak energy was necessary.* The agreement for $\Delta\tilde{\epsilon}$ is good. The calculated $\Delta\epsilon_1$ had to be shifted upward to obtain the agreement. We want to stress that, in the case of this structure compared to that of the first exciton, the roles played by the temperature variation of the peak energy and by the width are reversed. The resonance energy, the energy of the negative peak in $\Delta\epsilon_2$ (22.2 eV), is in perfect agreement with the results of Stephan.¹¹

The TM spectra for KCl are shown in Fig. 2. The line shapes of $\Delta\tilde{\epsilon}$ and of ΔEEL are very similar to those found for LiF, with the exception that now the structure is a multiplet. The three negative peaks in $\Delta\epsilon_2$ at 12.6, 13.8, and 14.7 eV occur at the same energies as the main peak in ϵ_2 and its two shoulders at higher energies.¹¹

According to the double-excitation theory,^{7,8} one expects that the peak energies of the structures in ϵ_2 and the loss function should move to higher energies upon cooling, by an amount approximately twice that of the first exciton peak. Since the creation of two excitons occurs via the electron-electron interaction, one expects that the linewidth should be only slightly temperature dependent. The experimental results disagree completely with these expectations for the alkali halides we have studied. Moreover, Lapeyre

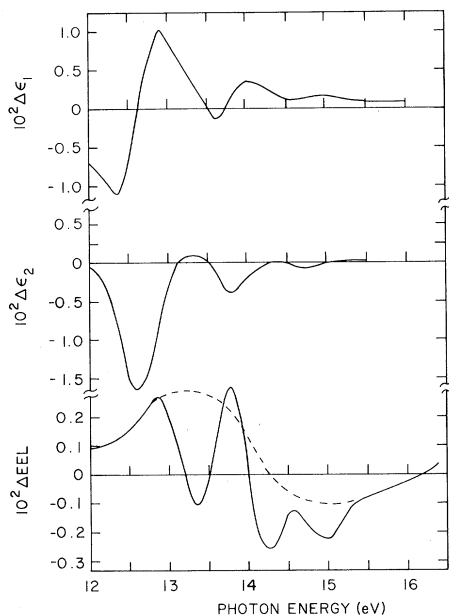


FIG. 2. Differential real and imaginary parts of the dielectric function, $\Delta\epsilon$, and $\Delta\epsilon_2$, and differential electron-energy-loss function, ΔEEL for KCl obtained by a Kramers-Kronig analysis of thermorefectance data. The dashed line is described in the text.

*et al.*¹⁹ did not observe double excitations in the photoemission spectrum of KCl. (Calculations, based on different approximations, of the intensity of double excitations gave results differing from each other by orders of magnitude.^{7,8,20})

The TM differential loss spectrum of LiF has two features in the region of the main electron-energy-loss peak: a negative peak at 25 eV and a dispersionlike structure, sketched by the dashed line in Fig. 1, crossing zero at about 24.6 eV. These two energies are in perfect agreement with the energies of the doublet observed by Gout and Pradal.⁹ Comparing these line shapes with the TM line shapes calculated for a peaked structure²¹ we see that the TM structure at 24.6 eV corresponds to a peak in the loss function which moves to higher energy upon cooling, while that at 25 eV corresponds to a peak which sharpens. The ΔEEL calculated from the $\tilde{\epsilon}$ and $\Delta\tilde{\epsilon}$ used to fit the experimental data as discussed above has a negative peak at 25.2 eV. We associate the structure at 25 eV in the electron-energy-loss function with the longitudinal counterpart of the oscillator peaking at 22.2 eV in ϵ_2 , possibly an exciton associated with the X or L points of the second conduction band.²² The longitudinal-transverse splitting is 3.6 eV,

using $\epsilon_c = 0.82$. This value of ϵ_c corresponds to the constant difference between the experimental¹¹ ϵ_1 and the ϵ_1 calculated for the oscillator above 24 eV. Below 24 eV, $\epsilon_c = \epsilon_{1,\text{expt}} - \epsilon_{1,\text{osc}}$ shows dispersion, crossing zero at about 22.5 eV. Looking at the energy bands of LiF,²² we see that the maximum energy for exciting an electron from the valence bands to the lower conduction band falls in this range. If we identify ϵ_c with the contribution to the dielectric constant from interband transitions, $\epsilon_c = \epsilon_{1,\text{ib}}$, the dispersion of ϵ_c becomes natural, since $\epsilon_{1,\text{ib}}$ increases as the square root of the energy above the M_3 critical point. Miyakawa has shown¹⁸ that in a two-band model, if the average oscillator strength of the interband transitions is large enough, the conditions for the loss function to peak can be satisfied above the M_3 critical point. In such a case a corresponding nearby structure in ϵ_2 is missing, as in the case of the plasma resonance of a free-electron gas, whereas peaks in the electron-energy-loss function due to excitons have corresponding structures in ϵ_2 .

The analogy can be carried further, since at energies much larger than the maximum interband energy, ϵ_1 approaches unity as E^{-2} . The excitation causing the peak in only the loss function corresponds to a longitudinal polarization wave formed by the collective excitation of virtual interband transitions, and thus has all the attributes of a "plasmon." When the temperature decreases, the density of electrons increases, and so does the free-electron plasma frequency. From the point of view of Miyakawa's theory,¹⁸ the same temperature dependence is expected. As the temperature decreases, the interband energies increase, and the plasmon solution shifts to higher energy. All these clues, together with our experimental results, strongly suggest associating the structure in EEL at 24.6 eV, instead of that at 25 eV,⁹ with the plasma resonance of the valence electrons. The shift to higher energy of the plasma frequency also gives a positive contribution to $\Delta\epsilon_1$, explaining why the calculated $\Delta\epsilon_1$ had to be shifted upward to fit the experimental one.

The angular dispersion of the plasmon according to Miyakawa's theory¹⁸ should follow that of the pair of bands in the neighborhood of the solution. For an M_3 critical point E should decrease as the momentum increases. New experimental results on the dispersion are needed to check our interpretation, and such measurements are in progress.²³

For KCl the Δ EEL spectrum shows three negative peaks superimposed on a dispersionlike structure, sketched with a dashed line in Fig. 2. The three minima at 13.35, 14.25, and 15.0 eV are interpreted as the longitudinal "excitons" associated with the three negative peaks in $\Delta\epsilon_2$. These structures follow a simple rule²⁴ found for a set of well-separated oscillators, according to which the transverse and longitudinal resonances must alternate. The energies of the first two negative peaks we measure in Δ EEL agree well with the peaks in the loss function, which must represent oscillatorlike transitions. The plasmon at about 14.3 eV is degenerate with them.

The phenomenon of a plasmon overlapping longitudinal excitonlike excitations seems to be a common occurrence in alkali halides. Although they are difficult to separate in conventional spectra, modulation spectroscopy allows their separation via line-shape analysis. These overlapping structures are due to two types of longitudinal excitations coupled by the longitudinal electric field. Such coupling usually pushes the resonant frequencies of the system apart from the uncoupled values.²⁵ The near degeneracy in alkali halides results from the background ϵ_1 due to interband transitions above and below the longitudinal resonance, which tends to hold the resonances in the loss function together, but weakens them. Part of ϵ_c arises from these transitions.

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